

## Development of Advanced Catalysts for Direct Methanol Fuel Cells

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### Objectives

- Reduce catalyst cost for direct methanol fuel cells
- Demonstrate the feasibility of reducing noble metal catalyst loading to less than 0.5 mg/cm<sup>2</sup>
- Develop a low-cost manufacturing technique for membrane electrode assembly (MEA) fabrication
- Identify potential non-noble metal catalytic systems

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost

### Approach

- Prepare multi-component thin film catalyst layers by direct current and radio frequency magnetron sputtering
- Identify a corrosion-resistant non-noble metal system
- Exploit nanophase properties of sputtered thin films based on Ni/Zr, Co/Zr, and other valve metal combinations
- Devise ways to control composition, microstructure, and electrochemical performance
- Characterize catalyst layers in half-cells and full cells
- Characterize catalyst layers by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for structural and electronic properties

### Accomplishments

- Prepared multicomponent combinatorial samples with unique non-equilibrium nanophase structure by sputter deposition
- Identified novel corrosion-resistant non-noble nanophase thin film catalyst layers based on nickel and zirconium
- Nickel/zirconium intermetallics with compositions less than 70% nickel found to be corrosion resistant under fuel cell conditions
- Nickel/zirconium layers have been found to protect base metal surfaces such as nickel in sulfuric acid
- Quaternary composition consisting of Pt-Ru-Ni-Zr enhances noble metal utilization in catalysts for methanol oxidation

## Future Directions

- Continue to study composition, morphology and electrochemical performance of Ni/Zr coatings
- Evaluate quaternary compositions of Ni-Zr-Pt-Ru to lower the amount of Pt-Ru and to tune electronic interactions
- Evaluate Co-Zr sputtered layers for methanol oxidation activity; Co has higher catalytic activity compared to Ni for many organic transformations
- Exploit morphological modification using ion-beam techniques for improving activity
- Correlate electronic properties of materials from extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) with catalytic properties

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## Introduction

Fuel cells offer the possibility of reduced emissions and high efficiency for transportation applications. Of the various fuel cells being considered, the direct methanol fuel cell (DMFC) is very attractive due to the key advantages of system simplicity and good transient response compared to reformate-air fuel cell systems. However, DMFCs currently require unsupported noble metal catalysts at high loadings of 2.5-4.0 mg/cm<sup>2</sup>, leading to a high catalyst cost of \$100-150/kW. Also, to keep the overall fuel cell cost low, the preferred method of catalyst application must be designed for manufacturing. Thus, cost presents a major obstacle to commercialization of DMFCs for transportation applications. Enhancement of the overall fuel cell efficiency is also necessary to meet the weight and volume requirements for transportation applications. The present research effort aims at addressing these key issues of cost and efficiency. The overall objective of the effort is to develop new low-cost electrocatalyst materials and new methods of preparing fuel cell electrodes that will reduce the amount of noble metal used and lead to overall cost reduction and improved performance of direct methanol fuel cells.

## Approach

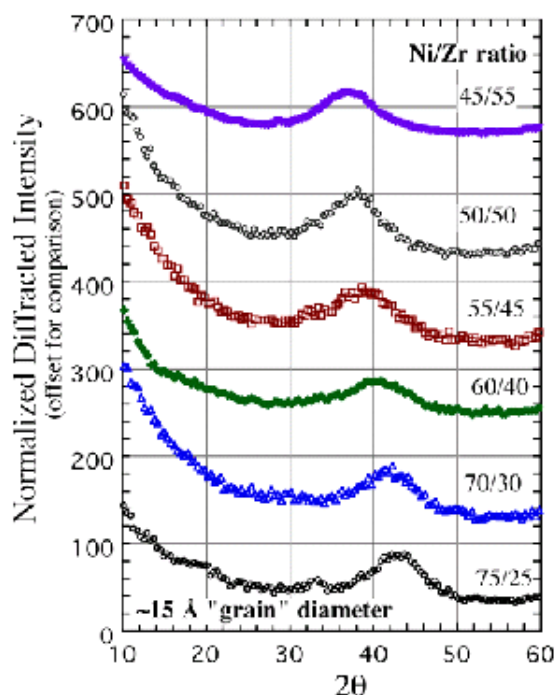
Using sputter-deposition, mixed compounds and multi-component alloys of virtually any composition can be readily deposited [1]. Specifically, non-equilibrium phases have unique properties compared to phase-separated intermetallics. Although non-noble metals such as nickel and cobalt are excellent for catalysis of hydrogenation and dehydrogenation

of organics, they are not stable in acidic media. Therefore, the possibility of creating multi-component alloys containing some mixture of Ni, Co, Zr, Pt, and Ru that are catalytically active and stable in the fuel cell environment has been investigated. The first studies conducted were on co-sputtered Ni-Zr films. Structure, corrosion resistance in acid, and electrochemical activity for methanol oxidation were then studied. A series of quaternary Ni-Zr-Pt-Ru samples were also fabricated and tested to examine the possibility of lower Pt/Ru loadings in the catalyst.

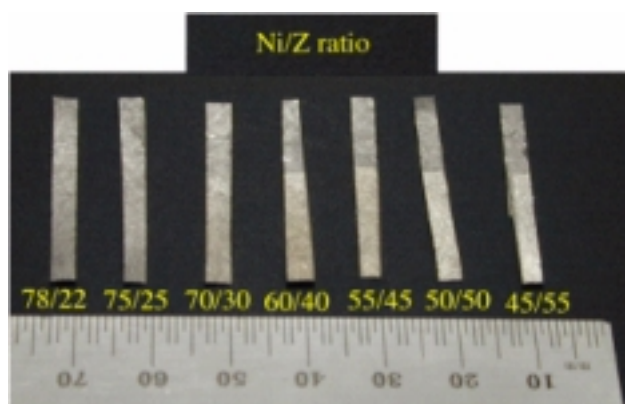
## Results

Investigations at JPL on sputter-deposited nanocrystalline Ni-Zr have shown that these bimetallic phases exhibit excellent corrosion resistance in 1 M sulfuric acid. Figure 1 contains results of X-ray diffraction from a series of combinatorially deposited Ni-Zr alloys with Ni/Zr atomic ratios ranging from 45/55 to 75/25. These data suggest that a single-phase nanocrystalline solid solution is obtained. Scherrer peak-broadening analysis indicates that the average grain size in these films is less than 2 nm. Based on the literature, such an amorphous/nanocrystalline type of structure is anticipated to be more corrosion resistant than similar materials with a polycrystalline microstructure.

Figure 2 shows an image of a series of samples consisting of Ni-Zr of varying composition deposited on carbon foil and immersed in a 1 M H<sub>2</sub>SO<sub>4</sub> solution for 24 hours. The photograph is visible evidence that films with Ni/Zr atomic ratios less than 70/30 remain intact and shiny, while those films with



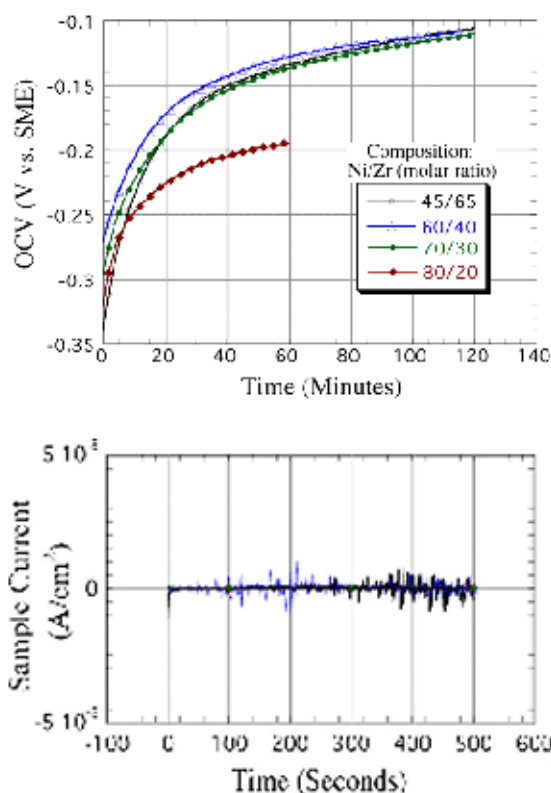
**Figure 1.** X-ray diffraction from a series of Ni/Zr films as deposited onto a Si wafer substrate. The data are consistent with that expected from a nanocrystalline Ni/Zr solid solution.



**Figure 2.** Image of Ni/Zr films sputtered onto carbon foil and immersed in 1 M  $\text{H}_2\text{SO}_4$  solution for 24 hours. The films with Ni/Zr atomic ratios less than 70/30 are still visible, while those films with higher Ni contents appear to have dissolved.

higher Ni content dissolve and leave behind a substrate with no coating.

Figure 3 (top) shows plots of open circuit potential (Voc) of various Ni/Zr film electrodes as a



**Figure 3.** (top) Plot showing Voc vs. time for Ni/Zr on C foil. Those with a Ni/Zr ratio lower than 70/20 had a higher potential vs. MSE compared to that observed from pure Ni, indicating chemical stability. (bottom) Potentiostatic current vs. time plots for a 40/60 Ni/Zr film under potentials ranging from 0.05 to 0.74 V vs. NHE. No measurable currents were detected.

function of time in de-aerated solutions of 1 M sulfuric acid. The open circuit potential values attained with all the compositions is much greater than 0.6 V vs. the mercury/mercurous sulfate reference electrode (MSE), suggesting that the surface is not evolving hydrogen and is extremely passive in contact with sulfuric acid. Also, data in Figure 3 (bottom) shows that there is essentially no cell current induced upon cell biasing with potentials ranging from 0.05 to 0.75 V vs. normal hydrogen electrode (NHE), confirming the corrosion resistance and absence of any significant faradaic process under applied anodic potentials. A film consisting of 40/60 Ni/Zr was used in a fuel cell anode as an under-layer for a sputtered Pt/Ru DMFC anode layer.

In this test, the anode structure consisted of a Torayâ carbon paper substrate, a 150-nm thick layer of Ni/Zr, and a 200 nm thick layer of Pt/Ru (50/50). This anode was combined with a Nafionâ membrane and a Pt-black cathode to form a membrane-electrode assembly that was tested as a direct methanol fuel cell. Figure 4 shows the performance of the fuel cell. The fuel cell performance was stable over several days of testing with no evidence of degradation, showing that the Ni/Zr was robust in the acidic fuel cell environment.

The results in Figure 4 also indicate that the Ni/Zr was sufficiently electrically conductive - an important criteria that needs to be satisfied by a corrosion-resistant layer to be considered for this type of application.

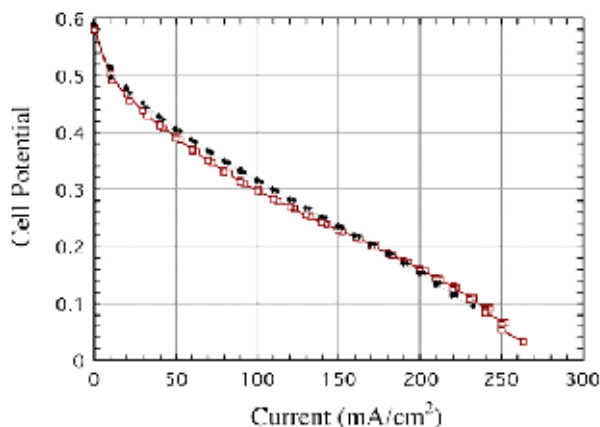
It is also possible for this new class of materials to be used to minimize the Pt/Ru loading by creating quaternary alloy systems that contain very small amounts of noble metal and are primarily composed of non-noble metals. One such possible system is co-sputtered Pt/Ru/Ni/Zr.

Results of polarization experiments in solutions of methanol/1 M sulfuric acid are shown in Figure 5. These results indicate that a catalyst layer that contains just 17% Pt exhibits the same current as that with 50 atomic % Pt, confirming the possibility of

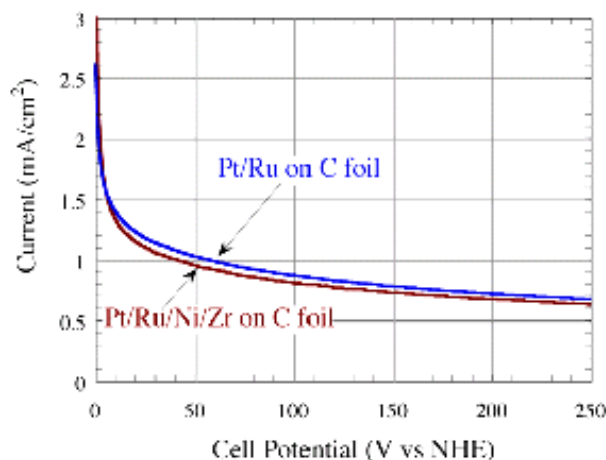
significantly lowering the noble metal content using non-noble metal additives such as Ni and Zr. Investigation of the electrochemical oxidation activity of these films, consisting of Pt-Ru-Ni-Zr, at elevated temperatures show that activity levels exceed those expected from plain sputtered PtRu (without Ni/Zr). The mechanisms driving this effect will be investigated in FY 2004.

## Conclusions

- Thin film corrosion-resistant and electrocatalyst layers consisting of non-noble metal combinations have been prepared by sputter deposition.
- As-deposited Ni-Zr films were found to be nanocrystalline in nature, with average grain sizes less than 2 nm in diameter.
- Ni/Zr films with nickel content greater than 40% were found to be corrosion-resistant in sulfuric acid and in the fuel cell environment.
- A direct methanol fuel cell comprising of a sputtered Pt/Ru (50/50) anode catalyst layer with an underlayer of 150 nm thick Ni-Zr was found to be stable over multiple days of testing.



**Figure 4.** Multiple current-voltage sweeps of a DMFC made using a Ni-Zr support layer on the anode. Though the Pt-Ru layer was not optimized for best performance, this test showed that a Ni/Zr support layer was compatible with a full fuel cell environment.



**Figure 5.** Potentiostatic data showing half-cell current vs. time for a Pt<sub>50</sub>Ru<sub>50</sub> film and a Ni<sub>16</sub>Zr<sub>36</sub>Pt<sub>17</sub>Ru<sub>31</sub> film sputtered on carbon foil. When held at 0.7 V vs. NHE in 1 M methanol, 1 M sulfuric acid at about 25°C, the observed current levels are very similar.

- Quaternary alloy mixtures of Pt-Ru-Ni-Zr have been found to have properties similar to Pt-Ru films with over three times the Pt content. This new class of alloy catalyst that consists of a large amount of non-noble metal with very small amounts of Pt seems to be extremely promising.

### **References**

1. DOE Labs Annual Report 2001.

### **FY 2003 Publications/Presentations**

1. S. R. Narayanan, J. Whitacre and C.K. Witham, "Advanced Catalysts for Direct Methanol Fuel Cells", Presentation at the DOE Lab Annual Merit Review, May 2003, Berkeley, CA.
2. "Nanocrystalline Corrosion-Resistant Layers Via Sputter Deposition." Manuscript in preparation, to be submitted to Journal of Power Sources in September 2003.

3. "Minimizing Pt Loading in Methanol Fuel Cells Using A Quaternary Pt-Ru-Ni-Zr Catalysis Layer." Manuscript in preparation, to be submitted to Journal of Electrochemistry in September 2003.

### **Special Recognitions & Awards/Patents Issued**

1. New Technology Report # 40415 titled "Corrosion resistant materials for fuel cells based on nanophase Nickel-Zirconium alloys", S.R. Narayanan, Jay Whitacre and T. I. Valdez, May 2003.
2. New Technology Report #20250: Sputter-deposited fuel cell electrodes and membranes with high performance and low-cost: A new technique for commercialization of fuel cells", B. Jeffries-Nakamura, W. Chun, S.R. Narayanan, R. Ruiz, August 1997.